

excess cold 1 *N* hydrochloric acid solution, and the ether layer was washed with water, dried, and the solvent was evaporated to give 13.0 g. of oil, whose infrared spectrum showed no absorption characteristic of tosylates or olefins. The oil was chromatographed on 300 g. of neutral activated alumina. Pentane eluted first 9-methylfluorene and then 7.7 g. (85%) of *meso*-VIII, m.p. 129–131°. Recrystallization of this material from ethanol gave m.p. 131–132°. A 20% solution of this material in carbon tetrachloride gave strong bands in the infrared at 3.27, 3.39, 3.43, 6.76, 6.88, 6.90, 7.26, 7.63, 8.21, 8.63, 9.72, 10.68 and 13.7 μ ; V.P.C. under condition "D" (see later section) showed a single symmetrical peak with retention time of 27.4 min.

Anal. Calcd. for $C_{35}H_{36}$: C, 92.05; H, 7.95. Found: C, 92.20; H, 7.88.

The (\pm)-isomer was prepared by the same procedure from a 100-ml. aliquot of the ether solution of organometallic reagent prepared above and 1.8 g. of ditosylate (\pm)-XXXVI. The oil obtained from the chromatograph column was recrystallized twice from 95% ethanol to give 1.2 g. (64%) of pure (\pm)-VIII, m.p. 110–111°. The infrared spectrum of the substance in carbon tetrachloride solution was essentially identical with that of its isomer; V.P.C. of the hydrocarbon under condition "D" showed a single symmetrical peak with retention time of 31.1 min. A synthetic mixture of *meso*- and (\pm)-VIII gave two completely resolved peaks in V.P.C. under conditions "D" whose retention times were 27.4 and 31.1 min.

Anal. Calcd. for $C_{35}H_{36}$: C, 92.05; H, 7.95. Found: C, 91.82; H, 8.19.

Preparation of Products of Runs 1–6 for Analyses.—Products of runs 1–5 were each reduced to XXXIII with excess lithium aluminum hydride in 50 ml. of ether in the usual way to give yields of 97–100%. These alcohols and that from run 6 were converted to their tosylates, which were free of alcohol or terminal olefin absorptions in the infrared. Yields ranged from 96–100%. Treatment of these tosylate esters with excess 9-lithio-9-methylfluorene gave hydrocarbon VIII as a mixture of diastereomers and 9-methylfluorene. Yields in this step were demonstrated to be essentially quantitative through V.P.C. comparisons with known mixtures. Solutions in carbon disulfide which were about 2% by weight in VIII were submitted to V.P.C. analysis (see next section).

After analysis of products of run 3, the material was chromatographed on 250 g. of neutral activated alumina. Elution with 1500 ml. of pentane gave 9-methylfluorene. An additional 300 ml. of pentane eluted 0.3 g. of material which by V.P.C. analysis under conditions "D" appeared to be mainly (+)-VIII. Recrystallization of this material from 95% ethanol gave 0.09 g. of (\pm)-VIII, m.p. 103–108°, undepressed by admixture with authentic compound. Elution of the column with 300 ml. of a 2% ether–98% pentane mixture gave 0.8 g. of approximately 50–50 mixture of diastereomers of VIII by V.P.C. analysis. Another 300 ml. of eluent gave 0.08 g. of material slightly rich in *meso*-VIII. Elution with 10% ether–90% pentane (300 ml.) gave material (0.3 g.) predominantly the *meso* isomer (V.P.C.

analysis). Recrystallization of the substance from 95% ethanol gave 0.10 g. of *meso*-VIII, m.p. 125–130°, undepressed by admixture with authentic *meso*-VIII. These experiments demonstrate the authenticity of the two syntheses of the diastereomers of VIII.

Analyses of Diastereomer Ratios of VIII Obtained from Products of Runs 1–6.—Conditions "D" (see next section) were used in the V.P.C. analysis. By use of a recorder with a disk-chart integrator, the area under the peaks produced by *meso*-VIII and (\pm)-VIII were measured for a 50%–50% synthetic mixture. The relative areas were constant over a large range of concentration of the original sample in carbon disulfide. However, this and other known mixtures demonstrated that the relationship between relative areas and diastereomer ratios was not constant. Hence a plot between % composition and relative peak area was made, and the ratio of diastereomers in the unknowns was determined graphically. The results are presented in Table I.

Vapor Phase Chromatography Conditions. Conditions "A."—A Perkin-Elmer model 154 vapor fractometer was used. The column was 75 cm. by 0.25 inch tubing packed with Chromosorb W upon which had been absorbed 2.5% of SE-30 silicone gum. The temperature of the column was 175° and the flow rate of helium was 80–85 ml./min. Retention times were: (2-(9-methyl-9-fluorenyl)-propene, 1.3–1.8 min.; 9,9-dimethyl-10-methylenepheneanthrene, 2.8–3.4 min.; 1-(9-methyl-9-fluorenyl)-1-propene, 1.8 min.; 1-(9-methyl-9-fluorenyl)-2-propanol, 2.6 min.; 2-chloro-1-(9-methyl-9-fluorenyl)-propane, 3.0–3.1 min.; 2-bromo-1-(9-methyl-9-fluorenyl)-propane, 3.5–4.0 min.; 9-ethyl-10-methylphenanthrene, 6.4–7.0 min.

Conditions "B."—A Loenco model 15 H gas chromatograph was used. The column was 6 ft. by 0.25 inch tubing packed with Chromosorb W upon which was absorbed 20% of SE-30 silicon gum. The preheater was at 225° and the column at 200°. The carrier gas was helium under a pressure of 12 p.s.i. Retention times were: 9,9-dimethylfluorene, 5.4 min.; 9-methylfluorene, 6.2–6.4 min.; 9-methyl-9-isopropylfluorene, 8.2–8.4 min.; 9-methylenefluorene, 9.2 min.; 9-fluorenone, 10 min.; 9-ethylidenefluorene, 16.0–17.0 min.; 9-(2-hexyl)-fluorene, 22.0 min.; 1-bromo-2-(9-methyl-9-fluorenyl)-propane, 25.6–26.4 min.

Conditions "C."—The same machine as in "B" was used. The column was 6 ft. by 0.25 inch tubing packed with Chromosorb W upon which had been absorbed 4% of SE-30 silicone gum. The preheater was at 300° and the column at 274°. The carrier gas was helium under a pressure of 12 p.s.i. Retention times were: 1-(9-methyl-9-fluorenyl)-1-(9-fluorenyl)-ethane, 6.8 min.; *meso*-2,3-dimethyl-1,4-bis-(9-methyl-9-fluorenyl)-butane, 10.1 min.; (\pm)-2,3-dimethyl-1,4-bis-(9-methyl-9-fluorenyl)-butane, 12.0 min.

Conditions "D."—An aerograph HY-Fi model 600 chromatograph (flame detector) with a 5 ft. by 1/8 inch column packed with firebrick upon which was absorbed 5% of SE-30 silicone gum was used. The preheater was above 280° and the column was at 265°. The carrier gas was nitrogen under a pressure of 15 p.s.i. Retention times were: (\pm)-2,4-dimethyl-1,5-bis-(9-methyl-9-fluorenyl)-pentane, 31.0 min., and *meso*-2,3-dimethyl-1,5-bis-(9-methyl-9-fluorenyl)-pentane, 27.4 min.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

Studies in Stereochemistry. XXXIV. Variation of Carbonium Ion Structure with Variation in Origin¹

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The 2-phenyl-2-butyl cation has been generated in glacial acetic acid at 50° by a variety of means, and the ratios to total olefin of the *cis*- and *trans*-2-phenyl-2-butenes and of 2-phenyl-1-butene were measured. With 2-phenyl-2-butyl chloride, acetate, alcohol, amine (diazotized) and hydrazine as starting materials, the amount of *cis*-olefin varied from 70–40%; *trans*, from 1–9%; terminal, from 16–60%. The more basic the leaving group, the lower the value of the ratio, *cis*/terminal. These results demonstrate that the leaving group remains associated with the carbonium ion formed long enough to affect seriously the behavior of that ion, and suggest that the leaving group in some cases abstracts a proton from the carbonium ion. The rates at which the three olefins went to their equilibrium mixtures and the compositions of the equilibrium mixtures were determined. The assumption was made that the same carbonium ion was generated by each olefin, and the proportion of each olefin produced by the carbonium ion was calculated to be 9% *cis*, 1% *trans* and 90% terminal. Under identical conditions 2-phenyl-2-butyl acetate gave 67% *cis*, 2% *trans* and 31% terminal. These data demonstrate that conformationally different 2-phenyl-2-butyl carbonium ions lose protons more rapidly than the conformations equilibrate.

In classical carbonium ion theory, one of the arguments presented for cationic intermediates is that the same ratios of different products are observed when

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only the leaving group is changed.³ Most of the early studies involved ethanol–water solvent systems, second-

(3) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 426; (b) K. A. Cooper, E. D. Hughes, C. K. Ingold and B. J. MacNulty, *J. Chem. Soc.*, 2038 (1948).

TABLE I
 PRODUCT COMPOSITION IN SOLVOLYTIC ELIMINATION REACTIONS OF 2-PHENYL-2-BUTYL-X IN GLACIAL ACETIC ACID AT $50 \pm 0.1^\circ$

Run	X	Concn. RX, M	Catalyst		Yld. olef., %	% cis	% trans	% term.
			Nature	Concn., M				
1	Cl ^a	0.1	TsOH ^b	0.011	90	70 ± 1	4 ± 1	26 ± 1
2	Cl ^a	.1	None	...	95	68 ± 3	9 ± 3	23 ± 3
3	OAc	.1	TsOH ^b	.009	..	67 ± 0.3	2 ± 0.2	31 ± 0.5
4	OAc	.1	None	53 ± .5	2 ± .5	45 ± .5
5	OH	.1	TsOH ^b	.010	..	65 ± .3	1 ± .3	34 ± .3
6	OH	.1	None	...	6	57 ± 2	0.6	42 ± 2
7	NH ₃ ⁺ Cl ⁻	.1	NaNO ₂	42 ± 1	7 ± 1	51 ± 1
8	NHNH ₂ ^c	.012 ^d	TsOH ^b	.009	<2	40 ± 0.3	0	60 ± 3

^a Product distribution corrected for errors due to unreacted starting material, for contamination of starting material with olefin, and for isomerization of olefin once produced by acid catalyst and by formed hydrogen chloride. ^b *p*-Toluenesulfonic acid. ^c Product distribution corrected for isomerization of olefin during reaction time. ^d Low substrate to catalyst ratio required by fact that hydrazine produced neutralized the *p*-toluenesulfonic acid.

 TABLE II
 EQUILIBRIUM MIXTURES OF CONJUGATED 2-PHENYLBUTENES

Olefin st. mat.	T, °C.	TsOH, M	Time, hr.	% cis	% trans	% term.
<i>cis</i>	100.4	0.90	1.0	78.7	18.3	3.0
<i>trans</i>	100.4	.90	1.0	77.7	18.4	3.9
Term.	100.4	.90	1.0	77.9	18.4	3.7
<i>cis</i>	100.4	.090	4.5	75.1	20.5	4.4
<i>trans</i>	100.4	.090	4.5	75.2	20.5	4.3
Term.	100.4	.090	4.5	76.2	20.2	3.6
<i>cis</i>	75.10	.90	5	79.1	17.6	3.3
<i>trans</i>	75.10	.90	5	78.4	18.4	3.2
Term.	75.10	.90	5	78.8	18.1	3.1
<i>cis</i>	75.10	.090	43	77.5	18.8	3.7
<i>trans</i>	75.10	.090	43	78.0	18.1	3.9
Term.	75.10	.090	43	77.9	18.7	3.4
<i>cis</i>	49.85	.90	50	81.0	16.0	3.0
<i>trans</i>	49.85	.90	50	80.6	16.2	3.2
Term.	49.85	.90	50	81.0	16.0	3.0
Extrapolation	50.2	.01	..	81.2 ± 0.8	15.8 ± 0.8	3.0 ± 0.1

 TABLE III
 INSTANTANEOUS SECOND-ORDER RATE CONSTANTS FOR ACID-CATALYZED OLEFIN ISOMERIZATIONS IN GLACIAL ACETIC ACID AT $50.10 \pm 0.05^\circ$

<i>cis</i> -2-Phenyl-2-butene			<i>trans</i> -2-Phenyl-2-butene			2-Phenyl-1-butene		
TsOH, M	Time, hr.	$k_{inst} \times 10^4$, l./m.s.	TsOH, M	Time, hr.	$k_{inst} \times 10^4$, l./m.s.	TsOH, M	Time, hr.	$k_{inst} \times 10^2$, l./m.s.
0.0092	21.92	1.12	0.0092	6.75	3.73	0.0101	0.42	1.99
.0101	24.43	1.07	.0101	13.83	3.82	.0092	.45	2.10
.0092	30.00	1.07	.0108	13.43	4.39	.0092	.62	1.92
.0101	37.58	0.91	.0092	13.75	3.51	.0101	.70	1.90
.0092	46.83	.81	.0108	16.53	3.75	.0092	.80	1.82
.0092	54.33	.72	.0092	19.92	3.16	.0101	1.00	1.85
.0101	62.05	.65	.0092	22.70	3.35	.0092	1.15	1.86
.0092	71.75	.69	.0101	23.52	3.55	.0092	1.28	1.66
.0092	81.08	.64	.0108	23.87	3.41	.0101	1.28	1.79
.0101	86.70	.54	.0108	37.10	3.51	.0092	1.50	1.86
.108	5.05	.77	.0101	37.42	3.19	.00101	2.40	2.20
.108	7.90	.57	.0092	38.75	3.44	.00101	4.48	1.90
.108	8.78	.55	.0092	45.17	3.23	.00101	6.40	1.96
.108	9.80	.56	.0101	47.32	3.41	.00101	8.50	1.90
...0092	63.50	2.86
...108	1.00	5.23
...108	1.88	4.48
...108	3.00	4.31
...108	3.98	4.20

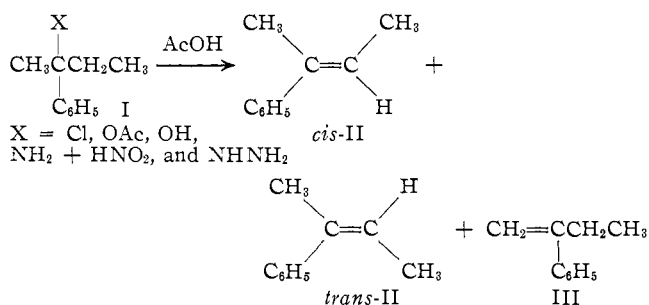
ary or tertiary carbonium ions and both substitution and elimination reaction products. Later studies involving bridged as well as open carbonium ions as intermediates in substitution, elimination and rearrangement reactions in acetic acid gave product ratios highly dependent on the character of the leaving group.⁴ Most of the latter examples involved a comparison of

products when leaving groups were changed from tosylate to amino groups.

The present investigation was undertaken to determine the effect of leaving group on the partitioning of the 2-phenyl-2-butyl cation between *cis*- and *trans*-2-phenyl-2-butene (II) and 2-phenyl-1-butene (III) in glacial acetic acid. The basicity of the leaving group was varied over a wide range (see formulas). In a complementary study, the 2-phenyl-2-butyl cation was

(4) For example, (a) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2129 (1952); (b) D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).

generated by addition of a proton to each of the three alkenes and, through kinetic analysis, the behavior of the carbonium ion produced without a leaving group was examined.



Results

The solvolytic elimination reactions were carried out in glacial acetic acid at $50.0 \pm 0.2^\circ$ on 2-phenyl-2-butyl acetate, chloride, alcohol, amine (diazotized) and hydrazine. The compositions of the olefinic products were determined by vapor phase chromatography, with the pure components as standards. In most runs, probable errors were $\pm 1\%$ or less. The source of the starting materials and the standard olefinic compounds is indicated in the Experimental. Table I records the results.

The three olefins underwent equilibration readily at 100° and 75° in glacial acetic acid, $0.09 M$ in *p*-toluenesulfonic acid, and at 100° , 75° and 50° in the same solvent with $0.90 M$ *p*-toluenesulfonic acid, but not at a reasonable rate at 50° with a $0.09 M$ concentration of acid. Plots of the logarithm of the concentrations of each olefin against the reciprocal of the temperature gave the expected straight line for those equilibrations carried out at the higher acid concentration. A slightly different line was described by the two points obtained at $0.09 M$ acid concentration. The equilibrium concentration of each olefin at 50° and $0.01 M$ acid was obtained by extrapolation of the data. These plots are set forth in Fig. 1, and the relevant data, actual and extrapolated, are recorded in Table II.

The kinetics of acid-catalyzed equilibration of the three olefins were studied by measuring the rate of disappearance of each isomer in glacial acetic acid at 50° with *p*-toluenesulfonic acid as added catalyst. Rates could be conveniently measured for *cis*- and *trans*-2-phenyl-2-butene at acid concentrations of approximately 0.01 and $0.10 M$, and for 2-phenyl-1-butene at 0.01 and $0.001 M$. Instantaneous second-order rate constants (first order in acid and first order in olefin) were measured for each olefin, and were found to change with time due to the back reaction in which the starting material is regenerated from its products. Table III records the results.

To correct for the back reactions, plots of the logarithms of the instantaneous rate constants against times were made and extrapolated to zero time. Reasonably straight lines were obtained for acid concentrations close to 0.01 and close to 0.1 for the *cis*- and *trans*-olefins, and for concentrations close to 0.01 and 0.001 for the terminal olefin (see Fig. 2). At the two higher concentrations of acid, the extrapolated rate constants varied somewhat with the tenfold change in acid concentration. At the two lower acid concentrations, the extrapolated rate constants were identical (see Table IV).

Discussion

Carbonium Ions Generated in Elimination Reactions.

The data of Table I demonstrate that the distribution

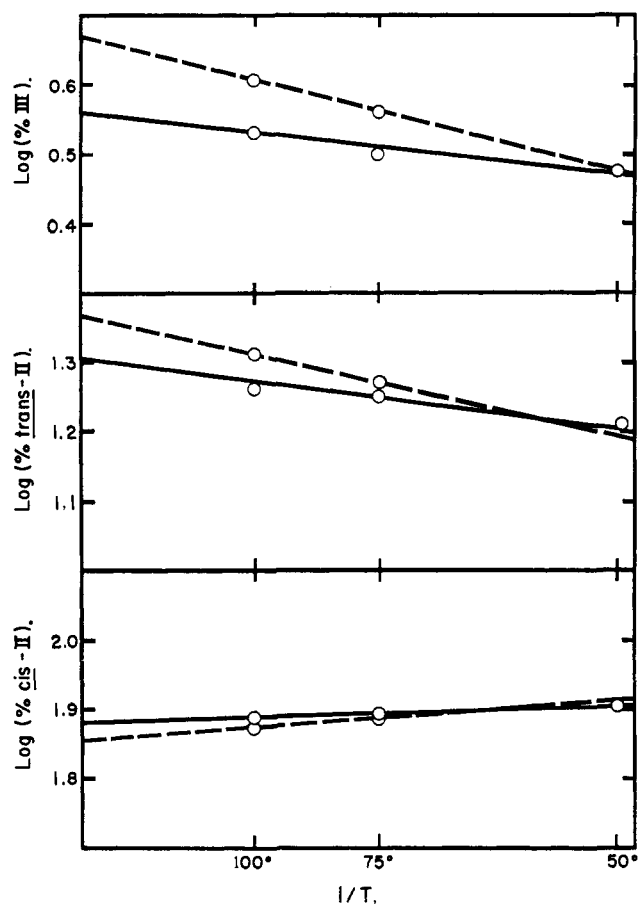


Fig. 1.—Plots of log % 2-phenylbutenes at equilibrium against $1/T$: top plots, 2-phenyl-1-butene; middle plots, *trans*-2-phenyl-2-butene; bottom plots, *cis*-2-phenyl-2-butene; solid lines, data obtained with $0.9 M$ *p*-toluenesulfonic acid; dashed lines, data with $0.09 M$ acid.

of products varies over a wide range, depending on the nature of the leaving group. The ratio *cis*/term. varies between extremes of 2.7 and 0.67, or by a factor of about 4. Even larger variations are visible in the ratios of *cis*/*trans* or term./*trans*. Thus the leaving

TABLE IV

EXTRAPOLATED RATE CONSTANTS FOR OLEFIN ISOMERIZATIONS

Olefin	TsOH, <i>M</i>	k_2 , l./m.s. ^a
<i>cis</i>	~ 0.01	$1.35 \pm 0.05 \times 10^{-4}$
<i>cis</i>	$\sim .1$	$0.92 \pm 1.8 \times 10^{-4}$
<i>trans</i>	$\sim .01$	$3.80 \pm 0.14 \times 10^{-4}$
<i>trans</i>	$\sim .1$	$4.9 \pm 1.1 \times 10^{-4}$
Terminal	$\sim .01$	$2.05 \pm 0.08 \times 10^{-2}$
Terminal	$\sim .001$	$2.05 \pm 0.13 \times 10^{-2}$

^a The uncertainties represent the standard deviations of the intercepts of the lines shown in Fig. 2.

group appears to play an important role in determining the product ratios. With chlorine as leaving group, the product ratios varied little when *p*-toluenesulfonic acid was added (runs 1 and 2). With this leaving group, the product was richest in *cis*-II and poorest in terminal olefin (III). With acetoxy or hydroxy as leaving group (runs 3–6), considerable variation in product ratios was observed when *p*-toluenesulfonic acid was present. This result strongly points to non-protonated leaving groups in the absence of *p*-toluenesulfonic acid, and protonated leaving groups in the presence of *p*-toluenesulfonic acid. With both acetoxy and hydroxyl, protonation of the leaving group increased the amount of terminal olefin at the expense of *cis*-II. The amount of *trans*-II was little effected. In run 7, a diazo-

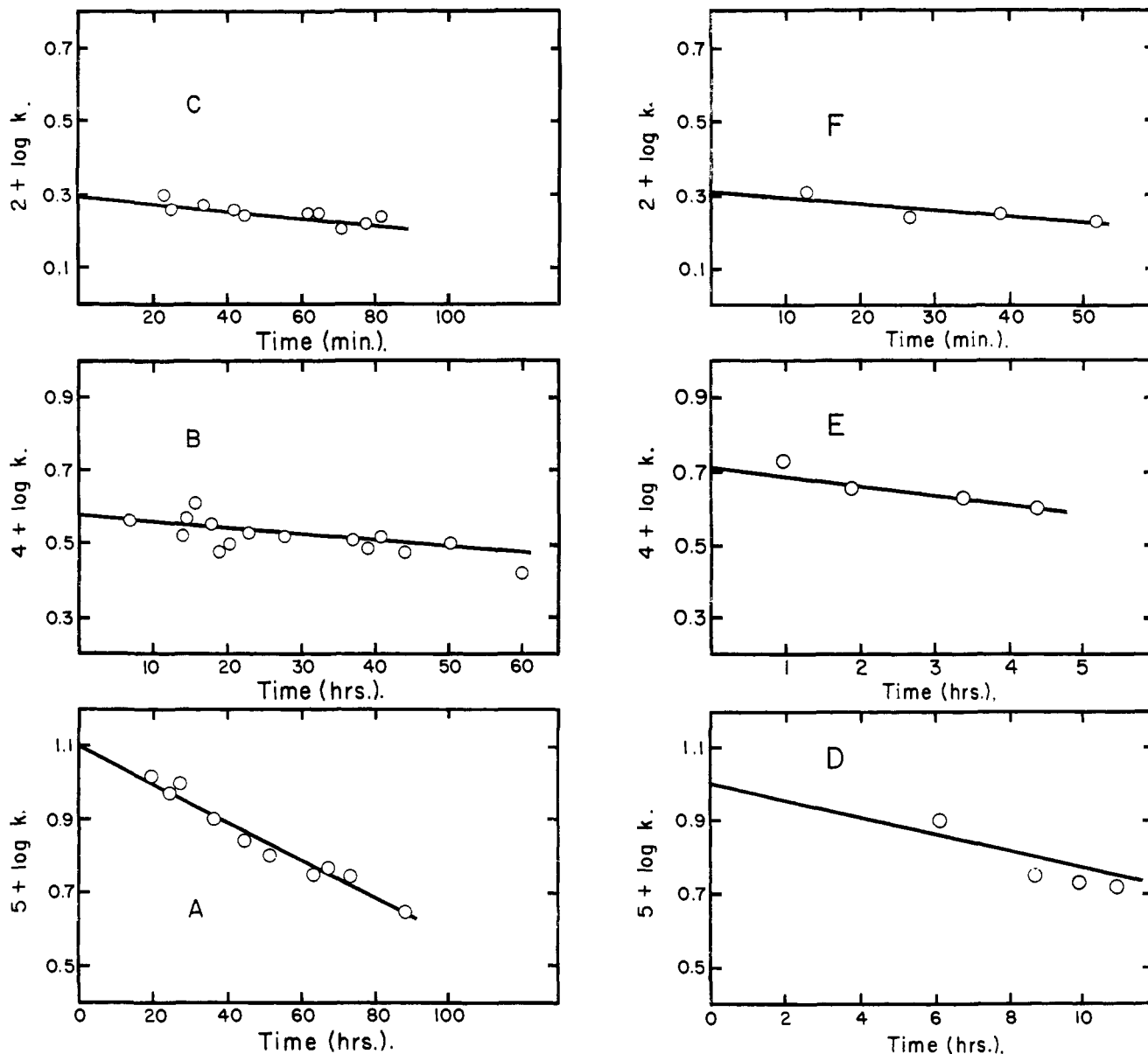


Fig. 2.—Plots of logarithms of the rates of isomerization of the 2-phenylbutenes against time: plot A, isomerization of *cis*-2-phenyl-2-butene in 0.01 *M* *p*-toluenesulfonic acid; plot B, isomerization of *trans*-2-phenyl-2-butene in 0.01 *M* *p*-toluenesulfonic acid; plot C, isomerization of 2-phenyl-1-butene in 0.01 *M* *p*-toluenesulfonic acid; plot D, isomerization of *cis*-2-phenyl-2-butene in 0.1 *M* *p*-toluenesulfonic acid; plot E, isomerization of *trans*-2-phenyl-2-butene in 0.1 *M* *p*-toluenesulfonic acid; plot F, isomerization of 2-phenyl-1-butene in 0.001 *M* *p*-toluenesulfonic acid.

tized amino group served as leaving group with its attendant ambiguity with regard to structure. A marked increase of terminal olefin at the expense of *cis*-II was observed. The extreme result was reached in run 8 with a protonated hydrazine leaving group. Here essentially no *trans*-II was formed and terminal olefin came to 60% and *cis*-II to 40%.

The generalization may be drawn from the results that the more basic the leaving group, the lower the *cis*-II/term. ratio. Even the diazotized amino group might possibly be compatible with the generalization if

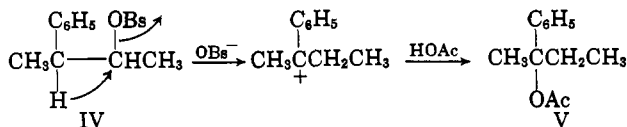
it reacted while still possessing a $\text{--NH}_2\text{--N}=\text{O}^+$ structure.⁵ Since these leaving groups differ little in their steric requirements, the conformational distributions of the carbonium ions they produce probably do not differ much. The difference in carbonium ion structure is accounted for by the differences in leaving groups, which remain associated with the carbonium ions after

(5) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt-Dryden, New York, N. Y., 1960, p. 175.

the covalent bond is broken. In most runs, once the covalent bond is broken, the leaving group is the most basic species in the medium, and would be expected to react rapidly with the carbonium ion, which is a strong acid. The more basic the leaving group, the faster becomes the proton transfer from carbonium ion to leaving group. Terminal olefin can be produced without conformational readjustment and should be favored by increased basicity of the leaving group, as is found.

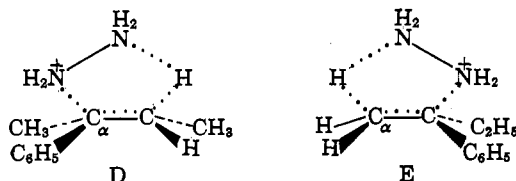
Previously⁶ it was observed that in acetolysis of optically pure *threo*- and *erythro*-3-phenyl-2-butyl *p*-bromobenzene sulfonate (IV) at 30°, the small amount of 2-phenyl-2-butyl acetate produced (V) by hydrogen migration was completely racemic. This result demonstrated that the 2-phenyl-2-butyl cation generated which produced acetate was long lived enough to become symmetrically solvated under conditions comparable to those of the present investigation. Thus the presence of leaving group near the carbonium ion is in-

(6) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2141 (1952).



indicated by the results of the elimination, but not by the rearrangement-substitution reaction. The steric requirements for proton transfer to give olefin are far less than for substitution, and possibly only the longer lived carbonium ions gave acetate.

Relationship between E1 and E_i Reaction Mechanisms.—Evidence has been presented here that in certain varieties of monomolecular elimination reactions, the leaving group serves as a base for proton abstraction. In the E_i reaction,⁷ the leaving group abstracts a proton from the β-carbon in the same transition state as the covalent bond at the α-carbon is broken. At some point in variation of system type and medium, the E_i and E1 mechanisms probably approach one another. Indeed, with some of the leaving groups employed in this investigation, a one-stage E_i reaction could well contribute to the products. For the protonated hydrazine group, transition states such as D and E can be envisioned for production of *cis*-II and III, respectively. On the basis of eclipsing effects, E would be more stable than D, and so any E_i contribution to products



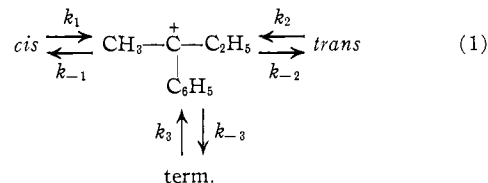
should favor terminal olefin. Although an E_i component may contribute to the results in runs 4, 6, 7 and 8, it is extremely improbable in runs 1, 2, 3 and 5 that the leaving group would become basic enough for proton abstraction before the covalent bond to C_α was broken. Even in the latter runs, enough variation in product ratios is evident to demonstrate that different intermediates are involved.

The results obtained here differ considerably from those obtained by the Hughes-Ingold school³ in 80% ethanol-water, in which ratios of products were essentially independent of leaving group (Cl, Br, I or (CH₃)₂S). In those studies the solvent was in all cases more basic than the leaving group, and therefore was able to compete successfully for the β-proton. In the present study, solvent was more basic than the leaving group only when alkyl chloride was employed as substrate.

Both electronic and steric explanations have been offered for the Saytzeff and Hofmann orientation rules for the elimination reactions.⁸ These rules would have been useless in predicting the products obtained in the present investigation, and enough exceptions are now known to impair seriously their usefulness even as a point of departure in discussions of reaction mechanism which involve carbonium ions.

Carbonium Ions Generated in Isomerization Reactions.—The kinetic data for olefin isomerization, coupled with the product data for the elimination reaction of 2-phenyl-2-butyl acetate under the same conditions, allow a test to be made of whether the same intermediates are involved in these processes. In treatment of the kinetics, the assumption is made that addition of a proton to the *cis*-, *trans*- and terminal olefins

produces the same carbonium ion, which partitions in the same way between the three olefinic products.



The rate constants for formation and disposal of the carbonium ion are defined in eq. 1. The *observed* rate constants for disappearance of the three olefins are defined as k_1' , k_2' and k_3' , for the *cis*-, *trans* and terminal olefins, respectively. These two kinds of rate constants are related by eq. 2, in which f_1 , f_2 and f_3 are defined as the fractions of *cis*-, *trans* and terminal-olefins formed, respectively, by loss of a proton from the carbonium ion. The observed rate of disappearance of *cis*-olefin (eq. 5) is equal to the rate at which *cis*-olefin

$$k_1 = k_1'/(1 - f_1); k_2 = k_2'/(1 - f_2); k_3 = k_3'/(1 - f_3) \quad (2)$$

goes to carbonium ion (eq. 3) minus the rate at which carbonium ion produces *cis*-olefin. Equation 5 simplifies to eq. 6.

rate at which *cis*-olefin produces carbonium ion =

$$k_1(cis)(TsOH) = \frac{(TsOH) k_1'(cis)}{1 - f_1} \quad (3)$$

Rate at which carbonium ion produces *cis*-olefin =

$$(TsOH) f_1 \left[\frac{k_1'(cis)}{1 - f_1} + \frac{k_2'(trans)}{1 - f_2} + \frac{k_3'(term.)}{1 - f_3} \right] \quad (4)$$

$$-\frac{d(cis)}{dt} = (TsOH) \left\{ \frac{k_1'(cis)}{1 - f_1} - f_1 \left[\frac{k_1'(cis)}{1 - f_1} + \frac{k_2'(trans)}{1 - f_2} + \frac{k_3'(term.)}{1 - f_3} \right] \right\} \quad (5)$$

$$-\frac{d(cis)}{dt(TsOH)} = k_1'(cis) - f_1 \left[\frac{k_2'(trans)}{1 - f_2} + \frac{k_3'(term.)}{1 - f_3} \right] \quad (6)$$

At equilibrium, the left and right hand sides of eq. 6 must be identically equal to zero, and eq. 7 follows, in which the subscript e denotes the equilibrium condition.

$$k_1'(cis)_e = f_1 \left[\frac{k_2'(trans)_e}{1 - f_2} + \frac{k_3'(term.)_e}{1 - f_3} \right] \quad (7)$$

Similarly eq. 8 and 9 can be derived. In effect, any one of eq. 7, 8 and 9 could be derived from the other

$$k_2'(trans)_e = f_2 \left[\frac{k_1'(cis)_e}{1 - f_1} + \frac{k_3'(term.)_e}{1 - f_3} \right] \quad (8)$$

$$k_3'(term.)_e = f_3 \left[\frac{k_1'(cis)_e}{1 - f_1} + \frac{k_2'(trans)_e}{1 - f_2} \right] \quad (9)$$

$$(cis)_e + (trans)_e + (term.)_e = 100\% \quad (10)$$

two, and hence eq. 10 is required for solution of three equations in the three unknowns, f_1 , f_2 and f_3 . It follows from eq. 10 that the concentration of isomers at equilibrium would be expressed in terms of percentages of total olefin. Values for f_1 , f_2 and f_3 were calculated by the method of successive approximation until the observed percentages of the three olefins at equilibrium were obtained. Thus, the 2-phenyl-2-butyl cation was calculated to produce 9% *cis*-2-phenyl-2-butene, 1% *trans*-2-phenyl-2-butene and 90% 2-phenyl-1-butene upon loss of a proton in glacial acetic acid, 0.01 M in *p*-toluenesulfonic acid at 50.2°.⁹

Under the same conditions, 2-phenyl-2-butyl acetate gave 67% *cis*, 2% *trans* and 31% terminal olefin (run 3).

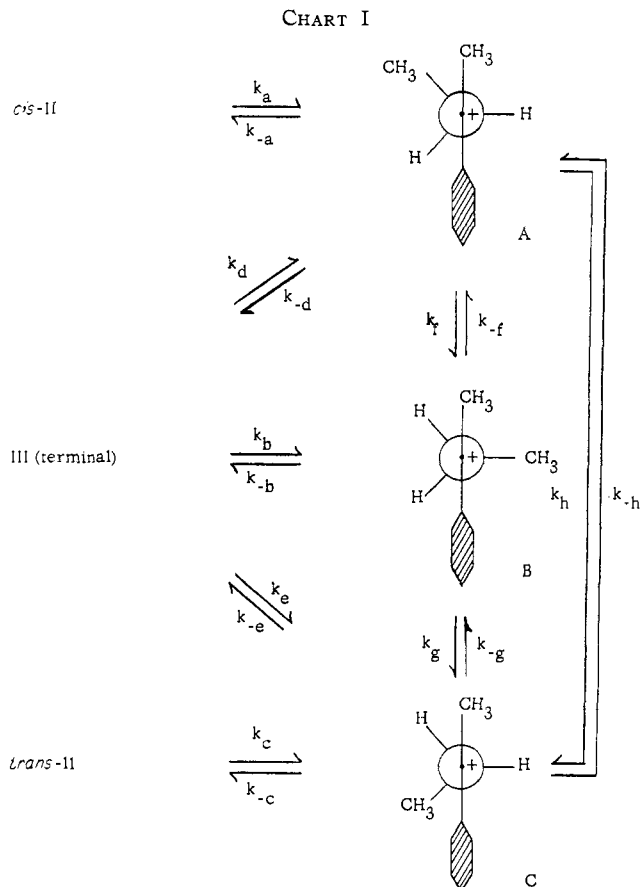
(9) At equilibrium at 50.2° and 0.01 M *p*-toluenesulfonic acid in glacial acetic acid, the composition of conjugated 2-phenylbutenes is 81% *cis*, 16% *trans* and 3% terminal. With $f_1 = 0.095$, $f_2 = 0.005$ and $f_3 = 0.900$, the calculated composition at equilibrium is 87% *cis*, 10% *trans* and 3% terminal. With $f_1 = 0.085$, $f_2 = 0.012$ and $f_3 = 0.903$, the calculated composition at equilibrium is 77% *cis*, 20% *trans* and 3% terminal. With $f_1 = 0.09$, $f_2 = 0.01$ and $f_3 = 0.90$, the calculated composition is 81% *cis*, 16% *trans* and 3% terminal.

(7) D. J. Cram in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 305.

(8) See ref. 7, p. 333, for a discussion.

Clearly, the olefin compositions from acetate and from the above calculation differ widely from one another. This discrepancy unequivocally demonstrates that all of the material in the isomerization and elimination reactions does not pass through the same intermediates. Otherwise the principle of microscopic reversibility would be violated.

If enantiomers are disregarded, the 2-phenyl-2-butyl cation possesses the three possible conformations A, B and C (Chart I). The terminal olefin III can arise directly from any of the three conformations, whereas *cis*- and *trans*-II can be produced directly only from conformations A and C, respectively. By inspection, it is obvious that $B > A > C$ in stability for much the same steric reasons that *cis*-II $>$ *trans*-II in stability. Clearly, mechanistic paths are available for olefin isomerization without involving equilibration of A, B and C. For example, if $k_{-d} > k_t$ or k_h , then *cis*-II could go to III with only A as intermediate. Likewise, if $k_{-e} > k_{-g}$ or k_{-h} , *trans*-II could provide III without C becoming equilibrated with A and B. In actual practice, it seems probable that the rate constants for the equilibration of intermediates A, B and C are of the same order of magnitude as those for proton loss of A, B and C, and that intermediates A, B and C become only partially equilibrated during the isomerization reaction.



At equilibrium, *cis*-II/*trans*-II/III is about 27/5/1. The lower stability of the terminal olefin is the usual result, and the greater steric inhibition of resonance in *trans*-II than in *cis*-II accounts for the greater stability of *cis*-II. With respect to rate of protonation, $k'_{\text{cis-II}}/k'_{\text{trans-II}}/k'_{\text{III}}$ is about 1/3/152. Thus the kinetic basicity of these hydrocarbons decreases with increasing thermodynamic stability of the olefin, as might be expected. Although $B > A > C$ in stability, the transition states for production of carbonium ion from III need not be arranged in a similar order, since an acetic

acid molecule must be included in these transition states. Since III gave *cis*-II with very little initial production of *trans*-II (observed while determining k_3'), it appears that the transition state for production of A and (or) B from III is more stable than that for C. It is worthy of note that in all cases less terminal olefin is formed than would be expected on purely statistical grounds, since any one of three methyl protons may be lost to form this isomer as opposed to only one specific proton for *cis*-II or *trans*-II.

Experimental

Analysis of Olefinic Products.—The three olefins *cis*- and *trans*-2-phenyl-2-butene (II) and 2-phenyl-1-butene (III) were prepared as previously,⁶ demonstrated to be pure to V.P.C. analysis (see below), and possessed the properties: *cis*-II, n_D^{25} 1.5403, b.p. 194°; *trans*-II, n_D^{25} 1.5193, b.p. 174°; III, n_D^{25} 1.5265, b.p. 183°. These olefins were subject to air oxidation, and therefore had to be stored over nitrogen in the cold. Analysis of olefin mixtures was accomplished with a Perkin-Elmer model 154 vapor fractometer with a 5-ft. column packed with 33% polyethylene glycol (Carbowax 1540) on firebrick (Chromosorb W) at 126° and with 20 p.s.i. helium as carrier gas. Retention times were: *cis*-II, 22 min.; *trans*-II, 10 min.; III, 14 min. The fraction of total olefin present as any given isomer was assumed to be the same as the ratio of the peak area for that isomer (estimated by means of a Disc Integrator attached to the instrument recorder) to the total peak areas attributable to olefinic products. The mixtures obtained from kinetic experiments were analyzed in 50-ml. portions of solution *ca.* 0.02 M in the olefinic products with anhydrous, redistilled pentane as solvent. Known mixtures of the olefins when analyzed identically to the kinetic samples indicated an analytical accuracy of $\pm 2\%$. Reproducibility of $\pm 0.5\%$ was obtained on repeated analysis of control samples.

Starting Materials.—The alcohol 2-phenyl-2-butanol was prepared as before⁶; n_D^{25} 1.5161. Conversion of this material to acetate was accomplished in 37% yield, n_D^{25} 1.4944. Absence of olefin and stability of the alcohol and acetate under analytical conditions of gas chromatography were demonstrated. The preparation of 2-phenyl-2-butyl chloride¹⁰ is as follows. Dry hydrogen chloride gas was bubbled through 2.0 g. of 2-phenyl-2-butanol for 3 min. at 25°. The product was dissolved in 3 ml. of pentane and cooled to -80° for 1 hr., during which time white crystals separated. The solution was decanted while still at -80° , dried at -80° , and the pentane was evaporated to a sirup (1.0 g.) under vacuum and was stored at 0°. Ultraviolet analysis of this material⁷ demonstrated virtual absence of *trans*-II and III in the sirup, and traces of *cis*-II. The amount of *cis*-II contaminant was found to be 2.3% from its ultraviolet absorption spectrum. The intensity of absorption at λ 244 μ of the contaminated chloride and pure *cis*-olefin were compared to give this percentage.

Solid 2-phenyl-2-butyl hydrazine oxalate (2.5 g.) obtained in a different investigation¹¹ was added to a solution of 1.6 g. of potassium hydroxide in 20 ml. of water. The solution was extracted three times with peroxide-free ether, the combined ether extracts were dried, and the ether was evaporated under vacuum in the absence of air. The residue was distilled at 1.4 mm. to give 1.0 g. of the desired compound, n_D^{25} 1.5355 (lit.¹¹, n_D^{25} 1.5349). A small amount of this material was dissolved in acetic acid, and the solution was shaken with pentane and water; V.P.C. analysis of the pentane extract demonstrated the complete absence of any olefinic material.

The hydrochloride salt of 2-phenyl-2-butylamine was prepared as previously¹² in 57% yield, m.p. 241–242° (lit.¹² m.p. 240–241°).

Kinetics of Isomerization of the Conjugated 2-Phenylbutenes.—All kinetic experiments were carried out under nitrogen using glacial acetic acid redistilled under nitrogen (b.p. 117–119°) and containing 2% acetic anhydride to ensure dryness. The concentration of *p*-toluenesulfonic acid present in the stock catalyst solutions was determined by titrating the solutions with sodium acetate in acetic acid, prepared by dissolving sodium carbonate as primary standard in glacial acetic acid. A few drops of saturated brom phenol blue in acetic acid was added as indicator to the solution being titrated, and the end-point was located by comparison with a solution of the indicator in acetic acid. In clean and dry 125-mm. Pyrex test-tubes were placed 2 ml. each of the stock catalyst solution and of the stock solution of the appropriate pure olefin 0.2 M in acetic acid, which had been stored in the

(10) A. Klages, *Ber.*, **35**, 3508 (1902).

(11) D. J. Cram, J. S. Bradshaw, W. Lwowski and G. R. Knox, *J. Am. Chem. Soc.*, **84**, 2832 (1962).

(12) D. J. Cram, C. A. Kingsbury and A. Langemann, *ibid.*, **81**, 5785 (1959).

refrigerator in the solid state and liquefied on the steam-bath under nitrogen. The tubes were sealed under nitrogen and placed in an oil-bath at the appropriate temperature. At the proper time each tube was removed, opened, and the contents were poured into 5 ml. of water which was promptly extracted with 2 ml. of pentane. The pentane extracts were washed with 5-ml. portions of 10% sodium hydroxide solution and then analyzed by gas chromatography. Table III records the results.

Equilibration of the Three Olefins.—The equilibration experiments were conducted with the same techniques employed in the kinetic experiments, and the results are recorded in Table II.

Elimination Reactions of 2-Phenyl-2-butyl Chloride (Runs 1 and 2).—Dry glacial acetic acid, or a dry solution of 0.011 *M* *p*-toluenesulfonic acid in acetic acid (4 ml.), was preheated to 49.85 ± 0.05°. Sufficient chloride was added to make each solution 0.1 *M* in substrate. After the appropriate times (see below), reaction aliquots were extracted with pentane, with water, dried and analyzed by V.P.C. In run 1 where *p*-toluenesulfonic acid was present, aliquots were taken after 9, 10, 11, 14 and 20 min., and in run 2 (absence of the same acid), aliquots were taken after 10, 15 and 20 minutes. The logarithm of each concentration found for each olefin was plotted against time and was extrapolated back to 0 time to correct for isomerization of olefin after it was formed. The amounts of unreacted chloride were determined after isolation by titrating with standard alcoholic silver nitrate solution; in no case was less than 90% of the chloride unreacted. The chloride was found to pyrolyze under the V.P.C. analytical condition to give 63.8% *cis*-II, 32.8% III, and 3.5% *trans*-II. The amount of each olefin contributed to the observed products by pyrolysis of unreacted starting material and by the small amount of *cis* contaminant in the starting chloride was calculated and deducted from the observed values. These corrections never exceeded 1.5%. The final results are recorded in Table I.

Elimination Reactions of 2-Phenyl-2-butyl Acetate (Runs 3 and 4).—In run 3, a stock solution of 0.009 *M* *p*-toluenesulfonic acid in dry glacial acetic acid was prepared, and to 4.00-ml. portions was added sufficient acetate (*ca.* 0.090 g.) to give solutions 0.10 *M* in substrate. Reaction mixtures were placed in a constant temperature bath at 49.85 ± 0.05°, and were quenched after 5, 7.5 and 10 min. by shaking them with water and pentane.

The pentane solutions were washed with dilute base, dried and submitted to V.P.C. analysis. The results of each of the 3 samples agreed within the probable errors of Table I. Run 4

was made in the same way except that no *p*-toluenesulfonic acid was present and a reaction time of 120 hr. was employed.

Elimination Reactions of 2-Phenyl-2-butanol (Runs 5 and 6).—In each of three test-tubes, 4 ml. of a stock solution 0.010 *M* in *p*-toluenesulfonic acid was preheated to 49.85 ± 0.05°. Sufficient substrate was then added (*ca.* 0.080 g.) to make the solutions 0.1 *M* in substrate. The reactions were quenched and worked up as with the acetate. Prior to analysis by gas chromatography, each sample was chromatographed on neutral alumina to remove any unreacted alcohol. The reactions run for 5 and 7.5 minutes yielded analyses agreeing within experimental error (see run 5, Table I).

In a sealed rate tube, 4 ml. of a solution 0.1 *M* in the carbinol in acetic acid was heated at 49.85 ± 0.05° for 150 hours, then quenched, extracted, chromatographed and analyzed as with the samples containing acid catalyst. Table I, run 6, records the results.

Deamination of 2-Phenyl-2-butylamine (Run 7).—A solution (4 ml.) 0.1 *M* in the amine hydrochloride in acetic acid was preheated to 49.85 ± 0.05° in the oil-bath and a stoichiometric amount (*ca.* 25 mg.) of sodium nitrite was added. After the nitrogen evolution subsided (*ca.* 2 min.), the white, cloudy mixture was poured into 5 ml. of water and 2 ml. of pentane to yield two clear phases. The pentane extract was worked up and analyzed as with the extracts from the other reactions. See run 7, Table I, for results.

Elimination Reaction of 2-Phenyl-2-butyl Hydrazine (Run 8).—To 16 ml. of a solution 0.009 *M* in *p*-toluenesulfonic acid in acetic acid which had been preheated to 49.85 ± 0.05° in the oil-bath was added enough of the pure hydrazine (32 mg.) to make the solution 0.012 *M* in substrate. After 15 minutes at the oil-bath temperature, the reaction was quenched with 15 ml. of water and extracted with 5 ml. of pentane. The pentane extract was washed with an equal volume of 10% sodium hydroxide and analyzed by the usual procedure.

A control experiment was run in which 2-phenyl-1-butene was substituted for the produced olefins, and pure hydrazine (Eastman Kodak Co. white label) for produced hydrazine or unreacted starting material. Identical conditions to those of the elimination reaction were employed, and the maximum extent of isomerization of produced olefin during the course of the elimination reaction was found to be 5%. This value was taken into consideration in evaluating the uncertainty in the product distribution from the elimination experiment.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

Studies in Stereochemistry. XXXV. Mechanism of E_i Reaction of Amine Oxides¹

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The first-order kinetics of the E_i (elimination) reaction of *threo*- and *erythro*-*N,N*-dimethyl-3-phenyl-2-butylamine oxide have been measured in tetrahydrofuran-water and dimethyl sulfoxide-water mixtures as well as in the pure solvents. Variations in rates as great as 10⁶ were observed as solvent was varied, the rates being lowest in water and highest in dry tetrahydrofuran. The rate was higher in wet dimethyl sulfoxide than in wet tetrahydrofuran because dimethyl sulfoxide acts as an internal drying agent and competes with aniline oxide for the water present. From pure tetrahydrofuran to 50 mole % tetrahydrofuran-50 mole % water as solvent, a linear relationship between Δ*F*[‡] and log (1/*N*_{H₂O}) was observed. From pure dimethyl sulfoxide to 20 mole % dimethyl sulfoxide-80 mole % water as solvent, a linear relationship between Δ*F*[‡] and *N*_{H₂O} was found. The reaction was completely stereospecific in the *cis* sense over temperature ranges from 0° to 138°. Ratios of *k*_{*threo*}/*k*_{*erythro*} ranged from 4.5 to 1.2, and *k*_{*conj.*}/*k*_{*nonconj.*} from 50 to 6 as solvent was changed.

Pyrolysis of esters, xanthates, carbonates, halides and amine oxides results in elimination reactions uncatalyzed by acids or bases, predominantly *cis* in steric direction and intramolecular in character.³ The term E_i is suggested for this class of reaction. Although the reaction in some cases occurs in the gas phase and appears to be one stage,⁴ the term E_i is meant to name the reaction class, whether or not all examples possess a common detailed mechanism. A recently discovered example of a dichotomy of mechanism was observed in

the pyrolysis of sulfoxides,⁵ which was *cis* and stereospecific in mechanism at about 80°, and was non-stereospecific at higher temperatures.

The present paper deals with a kinetic investigation of the Cope reaction, in which an amine oxide is pyrolyzed to produce an olefin and a hydroxylamine.⁶ Previous work has established that in amine oxides whose functional group is attached to branched carbon, the proportions of different products produced correlates with the number of hydrogens attached to the β-carbons.⁷ The reaction is highly stereospecific and

(1) This work was supported in part by the U. S. Army Research Office (Durham). Results were announced in a Communication to the Editor; D. J. Cram, M. R. V. Sahyun and G. R. Knox, *J. Am. Chem. Soc.*, **84**, 1734 (1962).

(2) National Science Foundation predoctoral fellow, 1961-1962.

(3) See D. J. Cram in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 305, for a review.

(4) (a) D. H. R. Barton, *J. Chem. Soc.*, 2174 (1949); (b) A. Maccoll and R. H. Stone, *ibid.*, 2756 (1961), and many previous papers.

(5) C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).

(6) Although the first example was first reported in 1898 by W. Werwick and R. Wolfenstein [*Ber.*, **31**, 1553 (1898)]; the scope, utility and general course of the reaction has been established by A. C. Cope and co-workers.

(7) A. C. Cope, N. A. LeBel, H. H. Lee and W. R. Moore, *J. Am. Chem. Soc.*, **79**, 4720 (1957).